

PATENT SPECIFICATION (11) 1 408 193

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(21) Application No. 31829/72 (22) Filed 6 July 1972
 (31) Convention Application No. 9943/71 (32) Filed 7 July 1971 in
 (33) Switzerland (CH)
 (44) Complete Specification published 1 October 1975
 (51) INT CL² C23C 13/04 C01F 7/30 C01G 25/02
 (52) Index at acceptance

1 408

C7F	1V1	1V2	2Z11A2X			
	2Z11AY	3U	4E	4F	4K	
B2E	193	19X	19Y	203	20Y	251
	327	338	349	368	378	41X
	41Y	518	528			
C1A	N40	N4AX				



(54) COATED CEMENTED CARBIDE ARTICLES

PATENTS ACT 1949

SPECIFICATION NO 1408193

In accordance with the Decision of the Principal Examiner, acting for the Comptroller-General, dated 16 March 1983 this Specification has been amended under Section 33 in the following manner:-

1 Page 5, delete line 26 insert We are aware of Patent No. 1344223 published after the priority date of the claims of this specification, but claiming two priority dates, of which one is before the priority date of the claims hereof. We make no claim to (i) a process of coating a cemented carbide substrate with a substantially fully dense coating consisting substantially of alpha aluminium oxide of from 1-20 microns thickness comprising passing an aluminium halide vapour, water vapour and hydrogen gas over the carbide substrate at a temperature of from 900° to 1250°C, the volume ratio of water vapour to hydrogen gas being between 0.025 and 2.0 or (ii) a cemented carbide article obtained directly by means of such a process. Subject to the aforesaid disclaimer, what we claim is:

THE PATENT OFFICE
 7 September 1983

Bas 253759/10

which layer has a thickness of less than 10 microns.

25 The present invention also provides a cemented carbide article at least a portion of a surface of which is coated with an adherent layer of refractory oxide selected from aluminium oxide, zirconium oxide, stabilized zirconium oxide and mixtures thereof, which layer has a thickness of less than 10 microns.

30 The process of the invention is particularly suitable for increasing the wear resistance of cemented carbide cutting tools which cannot be reground. The cemented carbide article preferably comprises (a) one or more of the carbides given above and (b) one or more of the binder metals given above.

35 The stabilized zirconium oxide used may be, for example, zirconium oxide stabilized by 10 mole per cent of magnesium oxide or 5 mole per cent of calcium oxide or at least one rare earth oxide in an appropriate ratio. The refractory oxides mentioned above may be used either alone or in the form of a mixture of these oxides. Preferably, the layer of refractory oxide is a layer of alpha aluminium oxide.

40 To increase the resistance to wear and consequently the useful life of a cemented carbide article by means of a coating of refractory oxide is quite an unexpected result. In fact, although it is well known that refractory oxides, particularly aluminium oxide and stabilized zirconium oxide, are very hard, it is equally well known that these oxides are more brittle than cemented carbide at least when these oxides are in the form of relatively large bodies of a size of at least some millimetres. Consequently, by coating the surface of a cemented carbide

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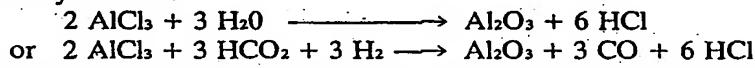
article with a layer of refractory oxide, normally there was not to be expected an adhesion of the coating on the surface of the article which would be sufficient to result in a durable improvement of the wear resistance of such surface.

5 The advantageous and unexpected result obtained is probably due to the careful choice of the thickness of the layer of refractory oxide. The thickness of the refractory oxide layer is preferably not less than 0.1 microns to obtain the greatest increase in the wear resistance. When the thickness of the refractory oxide layer is less than 0.1 microns it wears off rapidly.

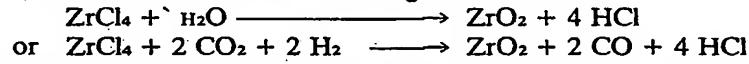
10 The layer of refractory oxide is preferably compact, coherent and homogeneous, and preferably has a thickness which is substantially uniform at least over the portions of the surface the wear resistance of which is to be increased. For depositing the refractory oxide layer on the surface of the cemented carbide article, any appropriate known method may be used. For example, particles of a refractory oxide powder which at least in part are in a liquid state may be cast on to the surface to be coated by some known appropriate means, for example, a plasma torch. To obtain a well adhering coating, the layer may be subjected to a 15 thermal treatment during and/or after the coating operation, thereby to increase the adhesion of the refractory oxide layer on the surface by diffusion with substitution of atoms. The deposition of the coating layer may also be effected by electrophoresis with a subsequent thermal treatment at a high temperature of the surface of the coating layer. In any case the thermal treatment is advantageously carried out at a temperature between 700 and 1200°C 20 for a time of at least half an hour. The thermal treatment may also be carried out for a duration of more than half an hour at a temperature of about 700°C. The oxide layer is preferably deposited from the gaseous state, particularly by evaporation and condensation under vacuum, by cathodic sputtering, or by deposition by chemical reaction in the gaseous phase, this latter method being usually referred to as "chemical vapour deposition" or 25 C.V.D. This latter method is preferably used in the process of the invention.

30 Among the various chemical reactions which may be used for depositing the refractory oxide coating layer, the reaction of a volatile halide, particularly a chloride, of the metal corresponding to the oxide, with water or with a mixture of carbon dioxide and hydrogen, is preferably used. Thus, when the layer of refractory oxide is a layer of alpha aluminium oxide, the layer of alpha aluminium oxide can be formed by passing an aluminium halide vapour and either water-vapour or a mixture of carbon dioxide and hydrogen over the surface of the article at a temperature sufficient for the aluminium halide to react to form alpha aluminium oxide.

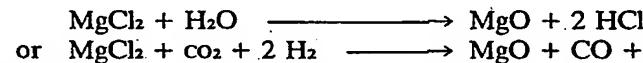
35 Thus, for example, for depositing an aluminium oxide coating layer one of the following two reactions may be used:



40 For depositing a coating layer of stabilized zirconium oxide (also called stabilized zirconium), on the one hand, one of the following two reactions:



45 and, on the other hand, one of the following two reactions for the formation of a stabilizing oxide may be used. The latter reaction is effected simultaneously with the corresponding reaction for the formation of zirconium oxide (merely by way of example, the two reactions are indicated hereafter for the case of the stabilizing oxide being formed by magnesium oxide):



50 In this case it is sufficient to select the proportion of zirconium chloride and of the element corresponding to the stabilizing oxide (here magnesium chloride) to obtain the desired proportion of stabilizing oxide (for example, 10 mole per cent in the case of magnesium oxide) in the stabilized zirconium.

55 As to the temperature and pressure conditions which permit the deposition of the refractory oxide coating layer, they must be selected according to the nature of the chemical compounds used as starting compounds. This selection can be made by one skilled in the art as it is evident from the abundant literature which has already been published on the conditions which are suitable for the deposition of various refractory oxides by chemical reaction in the gaseous 60 phase (cf. for example, the book "Vapour deposition" by C. F. Powell, J. H. Oxley and J. M. Blocher, published by John Wiley and Sons Inc., New York, London, Sidney).

For example, for depositing aluminium oxide by reaction of aluminium chloride with water, the following conditions are preferably chosen:

Temperature of the surface of the article to be coated with the aluminium oxide layer : 600
65 to 1200°C.

Feed rate of the gaseous hydrogen mixture (carrier gas)	
(amount reduced to 20°C and 760 torr)	400 cm ³ /min.
Aluminium chloride (AlCl ₃)	10 mg/min.
Water vapour	4 mg/min.

5 It was found that the major portion of the coating layer was formed by alpha aluminium oxide. 5

The composition of the cemented carbide cutting tool was as follows (in per cent by weight):

10	Cobalt	9.5	
	Titanium carbide	11.9	10
	Tantalum carbide	6	
	Niobium carbide	4	
	Tungsten carbide	68.6	

15 *Example 2* 15
An aluminium oxide coating layer having a thickness of 1 micron was deposited on a cemented carbide cutting tool of the same composition as that described in Example 1 by using said second reaction indicated above (reaction of aluminium chloride with carbon dioxide and hydrogen) under the following reaction conditions:

20	Time of depositing operation	7 minutes	
	Temperature	1000°C	20
	Overall pressure of the gaseous phase	50 torr	
	Feed rate of the gaseous mixture (amounts reduced to 20°C and at a pressure of 760 torr):		
25	Hydrogen	200 cm ³ /min.	
	Carbon dioxide	200 cm ³ /min.	25
	Aluminium chloride (AlCl ₃)	10 mg/min.	

It was found that the coating layer was formed by alpha aluminium oxide.

Example 3

30 The process as described in Example 2 was repeated, but with a time of 30 minutes for the depositing operation. Apart from this all the reaction conditions were the same as described in Example 2. In this manner an alpha aluminium oxide coating layer having a thickness of 6 microns is deposited on the cemented carbide cutting tool. 30

Example 4

35 The process as described in Example 2 was repeated, but after the depositing operation the cutting tool was kept at 1000°C. for 30 minutes under a hydrogen atmosphere. 35

Comparative cutting tests were carried out on a lathe with samples of the cutting tools coated with aluminium oxide as described in Example 2 and 3 and with cemented carbide cutting tools coated with a surface layer of titanium carbide. The samples consisted of hard steel of the following composition (in per cent by weight): 40

40	Carbon	0.96	
	Silicon	0.27	
	Manganese	0.25	
	Phosphorus	0.019	
45	Sulphur	0.015	45
	Chromium	0.15	
	Iron	the remainder	

50 These comparative tests have shown that the resistance to wear of the cutting tools produced by the process of the present invention is considerably improved with respect to the resistance to wear of the cutting tools produced by conventional methods. The results of the comparative test were as follows: 50

Series No. 1

55	Testing operation:	Turning	
	Test material:	Steel of the composition as indicated above	
	Cutting conditions: Speed	140 m/min.	55
	Feed	0.40 mm/revolution	
	Cutting depth	2.0 mm	
60	Different types of test material:	Life of cutting tool in minutes:	
	Cemented carbide of standard ISO P30	3.7	60
	Cemented carbide of standard ISO P10	13.0	
	Cemented carbide of standard ISO P30 coated with a layer of TiC having a thickness in the order of 5 microns	21.7	
65	Cemented carbide of standard ISO P30 coated with alpha aluminium oxide according to Example 3	43.1	65

binder metal.

15. A coated article as claimed in claim 12, 13 or 14, wherein the layer of refractory oxide has a thickness of not less than 0.1 microns.

5 16. A coated article as claimed in any one of claims 12 to 15, the cemented carbide article being a cutting tool which cannot be reground.

17. A coated cemented carbide cutting tool in accordance with claim 12, substantially as described in any one of the foregoing examples.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.